

Citation for published version:

García-Tuñón, E, Barg, S, Franco, J, Bell, R, Eslava, S, D'Elia, E, Maher, RC, Guitián, F & Saiz, E 2015, 'Printing in Three Dimensions with Graphene', *Advanced Materials*, vol. 27, no. 10, pp. 1-6.
<https://doi.org/10.1002/adma.201405046>

DOI:

[10.1002/adma.201405046](https://doi.org/10.1002/adma.201405046)

Publication date:

2015

Document Version

Peer reviewed version

[Link to publication](#)

This is the peer reviewed version of the following article: GarcíaTuñón, E. , Barg, S. , Franco, J. , Bell, R. , Eslava, S. , D'Elia, E. , Maher, R. C., Guitian, F. and Saiz, E. (2015), Printing in Three Dimensions with Graphene. *Adv. Mater.*, 27: 1688-1693, which has been published in final form at <https://doi.org/10.1002/adma.201405046>. This article may be used for non-commercial purposes in accordance with Wiley Terms and Conditions for Self-Archiving.

University of Bath

Alternative formats

If you require this document in an alternative format, please contact:
openaccess@bath.ac.uk

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

Take down policy

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

This is the accepted version of the following article: García-Tuñón, E., Barg, S., Franco, J., Bell, R., Eslava, S., D'Elia, E., Maher, R. C., Guitian, F. and Saiz, E. (2015), Printing in Three Dimensions with Graphene. Adv. Mater.. doi: 10.1002/adma.201405046, ***which has been published in final form at*** <http://dx.doi.org/10.1002/adma.201405046>

DOI: 10.1002/adma.201405046

Article type: Communication

Printing in three-dimensions with graphene

Esther García-Tuñón, Suelen Barg*, Jaime Franco, Robert Bell, Salvador Eslava, Eleonora D'Elia, Robert Christopher Maher, Francisco Guitian, and Eduardo Saiz*

Dr. Esther García-Tuñón, Dr Suelen Barg, Dr Salvador Eslava, Eleonora D'Elia, Prof. Eduardo Saiz

Centre for Advanced Structural Ceramics, Department of Materials, Imperial College London, London, SW7 2BP, United Kingdom

E-mail: egarciat@imperial.ac.uk, suelen.barg@imperial.ac.uk

Dr. Jaime Franco

Keramit S.L., Poligono Novo Milladoiro, A Coruña, Spain

Mr. Robert Bell

Department of Chemistry, University of Warwick, Coventry, CV4 7AL
United Kingdom

Dr Salvador Eslava

Department of Chemical Engineering, University of Bath, Bath BA2 7AY, United Kingdom

Dr. Robert Christopher Maher

The Blackett Laboratory, Imperial College London, Prince Consort Road, London, SW7 2BZ, United Kingdom

Prof. Francisco Guitian

Instituto de Ceramica de Galicia, Universidad de Santiago de Compostela, Spain

Keywords: 3D printing, graphene, responsive polymers, functionalization.

Despite the significant progress achieved in the development of 2D printable electronics with graphene,^[1-3] the additive manufacturing of three-dimensional graphene structures remains a challenge. However, the payoff could be very big as graphene optical, electrical, mechanical and thermal properties have the potential to open new engineering prospects well beyond electronics; from energy storage and transfer to sensing, catalysis, separation or structural and functional composites.^[3-7] A very apt technology for building macroscopic three-dimensional graphene structures is robotic assisted deposition. This technique is based on the continuous

extrusion of a suspension or ink with very specific rheological behavior. An effective way to achieve this behavior is to control accurately the interactions between graphene sheets in the suspension. In this respect, the use of chemically modified graphene (namely graphene oxide GO and its reduced form rGO) opens many possibilities. CMG sheets have tuneable surface chemistry, interfacial activity and solution processability making them a promising candidate for the integration of graphene into additive manufacturing.^[1,8-10] Chemically modified graphene has been used in the wet processing of porous monoliths and even wires from oil/water emulsions.^[9,11] However, to enable printing in three dimensions the filaments must have the right viscoelasticity to be able to maintain their shape after printing and to sustain the weight of a macroscopic printed part without deformation while exhibiting good adhesion to the previous layers. To address this challenge, in this work, we functionalize CMG with a responsive polymer (a branched copolymer surfactant, BCS) to create “responsive” sheets whose interactions in water can be regulated using an external stimulus, in this case pH.^[12-16] Using this approach it is possible to formulate water-based inks with viscoelastic properties optimized to print self-supporting 3D structures through nozzles with diameters ranging from 500 down to 100 μm (**Figure 1**). Additional treatments can be used to manipulate the chemistry and microstructure of the printed parts opening new possibilities in a wide range of key technological areas from energy storage to thermal management, sensing or catalysis.^[9,11,17]

GO is an atomically thin layer of carbon covalently bonded to different oxygen functional groups remaining from the chemical process used to exfoliate graphite.^[1] Hydroxyl and epoxy groups are distributed within the basal plane along with un-oxidized graphitic islands, and carboxylic groups on the edges.^[1] These carboxylic groups remain deprotonated at basic pH (Figure 1a).^[18] BCS is a copolymer composed of two main domains: poly methacrylic acid (PMA) and polyethylene glycol (PEG), which are cross-linked with ethylene glycol

dimethacrylate (EGDMA) to provide a branched architecture.^[12,13,15,16] Each polymer chain end contains 1-dodecanethiol (DDT), which offers multiple hydrophobic anchoring groups (supporting information and Figure 1a). The composition and architecture of BCS provide multiple functional groups that enable the adsorption of BCS molecules on GO in a water suspension. Attractive interactions between the hydrophobic DDT anchoring groups in the BCS structure (Scheme S1 and S2, Figure S1) and the hydrophobic graphitic islands of GO always take place, independently of pH range. In addition, there are adsorption mechanisms of BCS on GO that are pH-dependent as varying the pH modifies the ionization of GO^[18] and BCS functionalities (supporting information and Scheme S3). These interactions enable the BCS-functionalization of GO sheets.

BCS provides electrostatic and steric stabilization of the GO suspension at basic pH (>6.46) through: i) electrostatic repulsions between the MA functional groups; and ii) steric repulsions between the EG functionalities in BCS molecules functionalizing the basal plane of the sheets and the GO ionized edges (Figure 1b). As a result it is possible to prepare stable suspensions with relatively high GO contents (up to 3wt/v%). The GO/BCS suspensions at basic pH show a shear thinning behavior as well as predominantly elastic response at strains below 10% (Figure S8). Despite this viscoelastic behavior, the magnitude of the storage modulus is not high enough to hold the weight of free standing 3D objects printed by continuous extrusion. When the pH is decreased (below 6.46 - pKa of BCS molecules) the carboxylic groups in the BCS and the GO edges start to protonate enabling the formation of multiple hydrogen bonds. At pH below 3.88, all the carboxylic groups are protonated; multiple non-covalent interactions between MA and EG functional groups can take place inside the BCS molecules and between molecules.^[12,15] Non-covalent interactions can also take place between the MA and EG groups in BCS and the protonated carboxylic groups in GO edges. A gradual and homogeneous pH drop can be triggered by the addition of gluconic- δ -lactone (G δ L) that dissolves and then hydrolyses in water to gluconic acid.^[13,14] The consequence is the

formation of a GO/BCS 3D network linked by non-covalent interactions and an increase in the loss and storage modulus of more than 5 orders of magnitude (above 100kPa, **Figure 2b, c** and S8). This network forms a water-based ‘pseudo-gel’ with shear thinning behavior and a predominantly solid-like behavior at strains up to 1% (Figure S8, SI). Due to the non-covalent nature of the interactions the network-links can break down under shear (Figure S8) enabling the easy flow of the gel through nozzles with diameters down to 100 μm (Figure 2d, e). Once the stress is released the links can heal. The GO/BCS network recovers its ‘pseudo-gel’ structure and sets immediately after passing through the nozzle retaining the shape of the filament and holding the printed structure without deformation (Figure 1c-e). In this way it is possible to build 3D objects layer-by-layer using continuous extrusion (Figure 2d-e and supplementary movie 1).

Freestanding and stable GO three-dimensional filament piles, rings or woodpile structures with different shapes (Figures 1 to 4) were built in air through nozzles with internal diameters ranging from 100 to 500 μm using pressures between 1-4 bar depending on ink formulation. The printing speeds ranged between 4 and 10 mm s^{-1} . The inks contain from 1.75 to 3wt% GO and small amounts of additives (GO/BCS ratio of 6/1, G δ L/BCS ratio around 3.8/1, and GO/organics (BCS and G δ L) ratio of 1.3/1). The structures maintain their shape after printing and are strong enough to be handled. Subsequently, freeze drying is used to remove the water while preserving the 3D architecture and limiting shrinkage in order to maintain good dimensional control (supporting information).^[19-21] The process leads to 3D objects with smooth surfaces and microscopic porosity while maintaining fine printing features down to the micrometre range (**Figure 3**).

After printing, thermal treatments (e.g. at temperatures ranging from 900 to 1000 $^{\circ}\text{C}$ in Ar/H₂(10%) atmospheres) can be used to reduce GO while decomposing BCS and G δ L.^[22,23] Reduction is accompanied by 76 \pm 1% weight loss for lower concentrated inks (ranging from

1.7 to 2wt%GO) and $81 \pm 7\%$ weight loss for the more concentrated ones (ranging between 2.5 and 3wt%GO). Because the amount of additives is very small^[17,24] the degree of residual carbon left from additive decomposition will be very limited. After reduction, structures from higher-concentrated inks shrunk macroscopically over 4-7%. The measured shrinkage of the filament diameters ranges from 5 to 20% depending on the shape of the structure and the ink concentration. The resulting rGO objects are ultra-light and retain their shape, structural integrity and inner microstructure (**Figure 4**). EDS shows a significant decrease in oxygen content upon reduction and Raman spectroscopy confirms the formation of predominantly crystalline rGO (Figure 4).^[25] The electrical conductivity of the printed lines after reduction reaches values of 0.4 S cm^{-1} for filaments with densities around 6 mg cm^{-3} . These conductivities are comparable to those reported for other rGO porous networks (Figure S11).^[9,11,26,27]

All the structures have an elastomeric behavior and show between 96% and 90% recoverable deformation after 1 to 5 cycles of compression up to 20% strain (Figure 4), with stiffness and yield stress values in accordance to other porous graphene materials (Figure S11).^[9,11,28-30]

Prior to reduction the GO sheets are linked together by the BCS molecules that contribute to the mechanical response (Figure 4g). The reduction treatment burns out the BCS, decreases the density of the structures, and breaks the non-covalent links in the network (Figure 4h). As a consequence, non-reduced parts are stronger and stiffer than the reduced ones (Figure 4g and h). The estimated energy loss coefficients (energy dissipated in the material divided by the compression work in the first cycle) are of the order of 0.85 and 0.65 before and after thermal reduction respectively. These values are comparable to those measured for porous CMG monoliths.^[9]

The ability to print 2D materials in three dimensions has huge potential to open up multiple possibilities in the design and “on demand” fabrication of new devices. We have shown how functionalization with BCS can be used to formulate CMG inks with the viscoelastic response

needed to build practical three-dimensional structures with precision and reliability using robotic assisted deposition. The inks allow printing through nozzles as thin as 100 μm and their rheology could also be tailored for other processing technologies such as extrusion, gel or tape casting. Thermal annealing has been used to form electrically conductive rGO parts without compromising the structure and preserving the multifunctional properties of rGO. Alternatively, the mechanical stability of the printed parts may allow the use of additional treatments (e.g. chemical or electrochemical reduction) to further manipulate the properties without compromising the structure. By effectively extending the materials palette in AM technologies to include novel compounds, it will be possible to create new technological opportunities in the fabrication of devices and nanocomposites on demand for a wide range of applications in energy, environment, health or transportation.

Experimental Section

BCS was synthesized following the protocol described by Woodward et al (supporting information).^[15] Rhodamine was incorporated into the branched architecture in order to quantify BCS concentrations with UV-visible spectroscopy. Standard solutions of BCS-rhodamine (BCSr) with concentrations ranging from 0.001 to 5 wt/v% were prepared in distilled water at pH 8 and measured in UV-visible spectrometer to obtain the calibration curve by plotting the absorbance vs. concentration at 566nm. Afterwards, the supernatants of GO/BCSr suspensions containing 0.2 wt% GO sheets and increasing amounts of BCSr (ranging from 0.001 to 5 wt/v%) were analyzed by UV-visible spectroscopy after centrifugation. The BCS adsorption isotherm on GO sheets was determined by comparing the UV-visible absorbance at the excitation wavelength for rhodamine (566 nm). GO solutions were prepared using a modified Hummers method (supporting information).^[31] GO/BCS solutions were prepared by mixing different amounts of BCS stock solution (8wt/v% in distilled water at pH 12) and GO suspension, keeping the GO/BCS ratio 6 to 1.

Printable GO networks were prepared by lowering the pH of GO/BCS suspensions, with glucono- δ -lactone (G δ L). The total content of organics was fixed at 1.3 (GO/organic content (BCS and G δ L)).

The flow behavior and viscoelastic properties of GO suspensions (pH>8) and inks (pH<5) were measured in a Discovery Hybrid Rheometer HR1 (TA Instruments). The flow experiments were carried out with a parallel plate (\varnothing =40 mm) and a solvent trap cover under steady sensing. The self-assembly process was monitored by measuring the viscoelastic properties (G' , G'') over time, immediately after lowering the pH of GO-BCS suspensions. The oscillation measurements (time sweeps with fixed frequency (0.1 Hz) and strain (γ =1%)) were applied immediately after adding the pH trigger. A solvent trap cover prevented evaporation of the solvent, while the axial force control allowed identifying changes in volume as well as automatically adjusting the gap. Viscoelastic fingerprints and linear viscosity region (LVR) were evaluated with stress-controlled amplitude sweeps at a fixed frequency of 396 rad s⁻¹, and stress-controlled frequency sweeps at a fixed strain of 0.15% (supporting information).

GO/BCS inks were used to print 3D objects using a robotic deposition device (Robocad 3.0, 3-D Inks, Stillwater, OK). The diameter of the printing nozzles ranged from 100 to 500 μ m (EFD precision nozzles, EFD, East Providence, RI). The inks were prepared at least 24 hours before printing to ensure a stable rheological response. The pressure is regulated during printing in air to maintain constant ink flow.

3D printed GO structures were frozen in liquid nitrogen and subsequently freeze-dried (Freezone 4.5, Labconco Corporation). Once dried, samples were reduced in a tubular furnace (Carbolite Furnaces) at 950°C in a 10%H₂/90%Ar atmosphere.

The microstructure and chemical composition were studied by field emission scanning electron microscopy on a LEO Gemini 1525 FEGSEM equipped with an energy dispersive

spectroscopy (EDS) microprobe (INCA Sight Oxford-instruments, UK). Raman spectroscopy was performed using a Renishaw RM2000 equipped with a 514 nm laser.

The mechanical tests were carried out in a Zwick universal testing machine with a maximum load of 2 kN. The 3D structures were subjected to cyclic compression in the direction perpendicular to the printing plane: up to 5 cycles at 10% and 20% strain, with a holding period of 30s under position-controlled movement of 1 mm min⁻¹.

A standard 4-point probe method was used for conductivity measurements. The current was generated via a bench top PSU and kept at a constant direct current of 10 mA. Two electrodes were placed through the sample at constant distance to monitor the voltage drop through the sample. The results were derived via standard equations for electrical conductivity and resistivity in DC.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

The authors would like to acknowledge the EPSRC grant Graphene 3D Networks (EP/K01658X/1). S.B. would like to acknowledge the European Commission (FP7 Marie Curie Intra-European Fellowship ACIN). S.E. would like to acknowledge EPSRC grant Engineering with Graphene for Multifunctional Coatings and Fiber-Composites EP/K016792/1. E.S. and E.G.T. would like to acknowledge the support of RFEC-ATL, ONRG, and DARPA.

Received: ((will be filled in by the editorial staff))

Revised: ((will be filled in by the editorial staff))

Published online: ((will be filled in by the editorial staff))

- [1] F. Kim, L. J. Cote, J. Huang, *Adv. Mater.* **2010**, 22, 1954.
- [2] S. Wang, P. K. Ang, Z. Wang, A. L. L. Tang, J. T. L. Thong, K. P. Loh, *Nano Lett.* **2010**, 10, 92.
- [3] F. Torrisi, T. Hasan, W. Wu, Z. Sun, A. Lombardo, T. S. Kulmala, G.-W. Hsieh, S. Jung, F. Bonaccorso, P. J. Paul, D. Chu, A. C. Ferrari, *ACS Nano* **2012**, 6, 2992.
- [4] A. K. Geim, K. S. Novoselov, *Nat Mater* **2007**, 6, 183.
- [5] G. Eda, G. Fanchini, M. Chhowalla, *Nature Nanotech* **2008**, 3, 270.
- [6] S. Stankovich, D. A. Dikin, G. H. B. Dommett, K. M. Kohlhaas, E. J. Zimney, E. A. Stach, R. D. Piner, S. T. Nguyen, R. S. Ruoff, *Nature* **2006**, 442, 282.
- [7] M. D. Stoller, S. Park, Y. Zhu, J. An, R. S. Ruoff, *Nano Lett.* **2008**, 8, 3498.
- [8] C. Cheng, D. Li, *Adv. Mater.* **2012**, 25, 13.
- [9] S. Barg, F. M. Perez, P. do V Pereira, N. Na, R. Maher, E. Garcia-Tunon, S. Eslava, S. Agnoli, C. Mattevi, E. Saiz, *Nature Communications* **2014**, 5, 1.

- [10] S. Naficy, R. Jalili, S. H. Aboutalebi, R. A. Gorkin III, K. Konstantinov, P. C. Innis, G. M. Spinks, P. Poulin, G. G. Wallace, *Materials Horizons* **2014**, *1*, 326.
- [11] L. Qiu, J. Z. Liu, S. L. Y. Chang, Y. Wu, D. Li, *Nature Communications* **2012**, *3*, 1241.
- [12] J. V. M. Weaver, S. P. Rannard, A. I. Cooper, *Angew. Chem.* **2009**, *121*, 2165.
- [13] D. E. García-Tuñón, S. Barg, R. Bell, J. V. M. Weaver, C. Walter, L. Goyos, E. Saiz, *Angew. Chem. Int. Ed.* **2013**, *52*, 7805.
- [14] R. T. Woodward, L. Chen, D. J. Adams, J. V. M. Weaver, *Journal of Materials Chemistry* **2010**, *20*, 5228.
- [15] R. T. Woodward, C. Hight, U. Yildiz, N. Schaeffer, E. M. Valliant, J. R. Jones, M. M. Stevens, J. V. M. Weaver, *Soft Matter* **2011**, *7*, 7560.
- [16] R. T. Woodward, J. V. M. Weaver, *Polym. Chem.* **2011**, *2*, 403.
- [17] L. Zhang, F. Zhang, X. Yang, G. Long, Y. Wu, T. Zhang, K. Leng, Y. Huang, Y. Ma, A. Yu, Y. Chen, *Scientific Reports* **2013**, *3*, 1408.
- [18] B. Konkena, S. Vasudevan, *J. Phys. Chem. Lett.* **2012**, *3*, 867.
- [19] J. A. Lewis, *Journal of the American Ceramic Society* **2000**, *83*, 2341.
- [20] J. E. Smay, J. Cesarano, J. A. Lewis, *Langmuir* **2002**, *18*, 5429.
- [21] J. J. Guo, J. A. Lewis, *Journal of the American Ceramic Society* **1999**, *82*, 2345.
- [22] A. Bagri, C. Mattevi, M. Acik, Y. J. Chabal, M. Chhowalla, V. B. Shenoy, *Nature Chem* **2010**, *2*, 581.
- [23] S. Pei, H.-M. Cheng, *Carbon* **2012**, *50*, 3210.
- [24] V. Dua, S. P. Surwade, S. Ammu, S. R. Agnihotra, S. Jain, K. E. Roberts, S. Park, R. S. Ruoff, S. K. Manohar, *Angew. Chem. Int. Ed.* **2010**, *49*, 2154.
- [25] L. G. Cançado, A. Jorio, E. H. M. Ferreira, F. Stavale, C. A. Achete, R. B. Capaz, M. V. O. Moutinho, A. Lombardo, T. Kulmala, A. C. Ferrari, *Nano Lett.* **2011**, 3190.
- [26] X. Zhang, Z. Sui, B. Xu, S. Yue, Y. Luo, W. Zhan, B. Liu, *Journal of Materials Chemistry* **2011**, *21*, 6494.
- [27] Z. Chen, W. Ren, L. Gao, B. Liu, S. Pei, H.-M. Cheng, *Nat Mater* **2011**, *10*, 424.
- [28] M. A. Worsley, S. O. Kucheyev, J. H. Satcher Jr, *Applied Physics Letters* **2009**.
- [29] X. Xie, Y. Zhou, H. Bi, K. Yin, S. Wan, L. Sun, *Scientific Reports* **2013**, *3*, DOI 10.1038/srep02117.
- [30] H. Hu, Z. Zhao, W. Wan, Y. Gogotsi, J. Qiu, *Adv. Mater.* **2013**.
- [31] M. Hirata, T. Gotou, S. Horiuchi, M. Fujiwara, M. Ohba, *Carbon* **2004**, *42*, 2929.

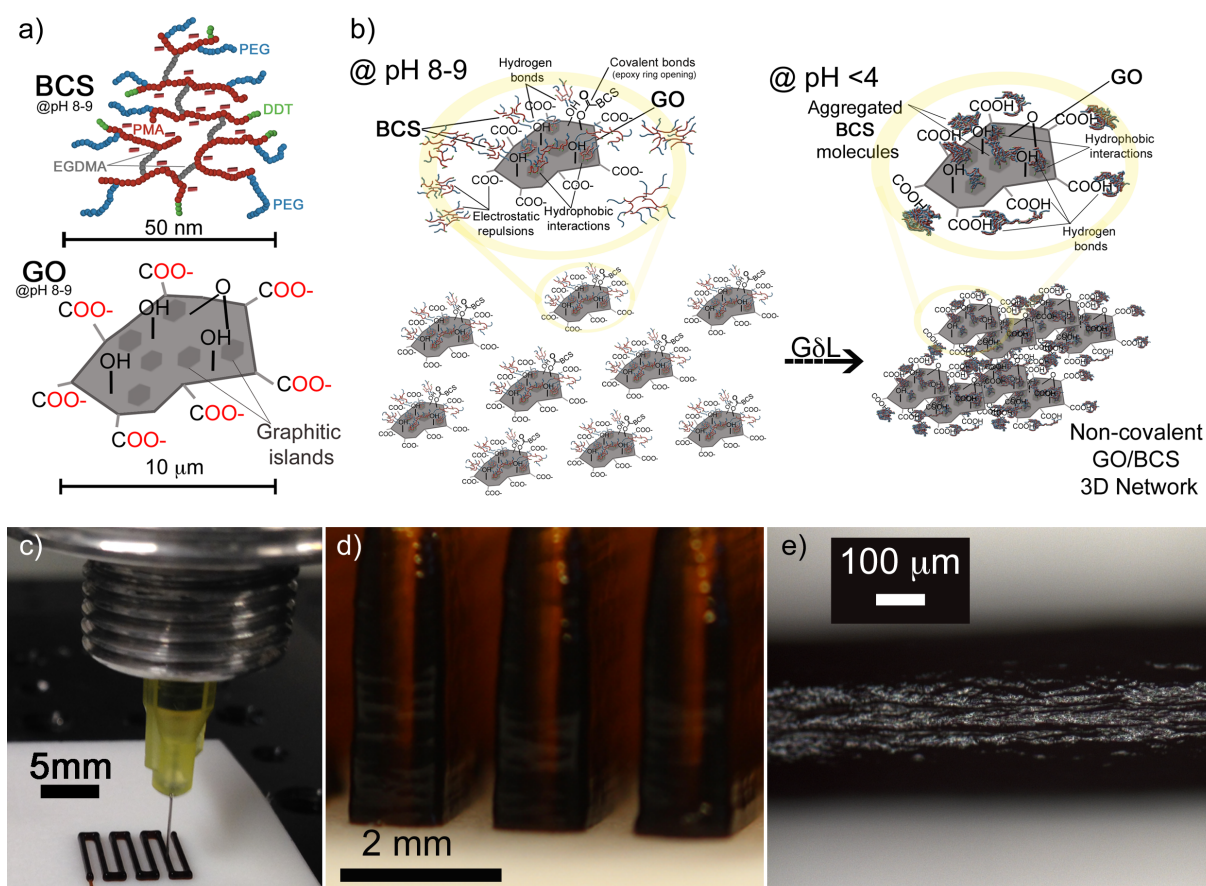


Figure 1. a) Simplified schematics depicting the proposed BCS and GO structures at basic pH (>6.46). Top - Composition and architecture of BCS: cross-linked PMA and PEG domains provide a branched structure with multiple hydrophobic anchoring groups DDT. Bottom – GO structure showing the distribution of functional groups on the basal plane (hydroxyl, epoxy and un-oxidized graphitic islands) and edges (carboxylic groups). b) Sketch of the directed assembly mechanism. BCS molecules attach to the basal plane of GO sheets at basic pH by: i) covalent bonding due to epoxy ring by nucleophilic attack, ii) hydrogen bonds between the GO hydroxyl groups and the EG groups in BCS, and iii) hydrophobic interactions between DDT anchoring groups and graphitic islands. When lowering the pH below ~4, the protonation of COO^- groups in BCS branches and GO sheets leads to the establishment of multiple hydrogen-bonds and directs the assembly of GO sheets into a 3D network. c) Building a filament pile through a 100 μm nozzle with a low concentrated GO/BCS ink (1.75wt%). d) Macroscopic image showing the fine details of piled up lines printed by continuous extrusion through a nozzle with a diameter of 100 μm. e) Optical microscopy of a filament immediately after printing through a 100 μm nozzle. Certain degree of filament expansion is observed. An increase of solid concentration of the ink helps preserving filament dimensions by increasing its “strength” (G')).

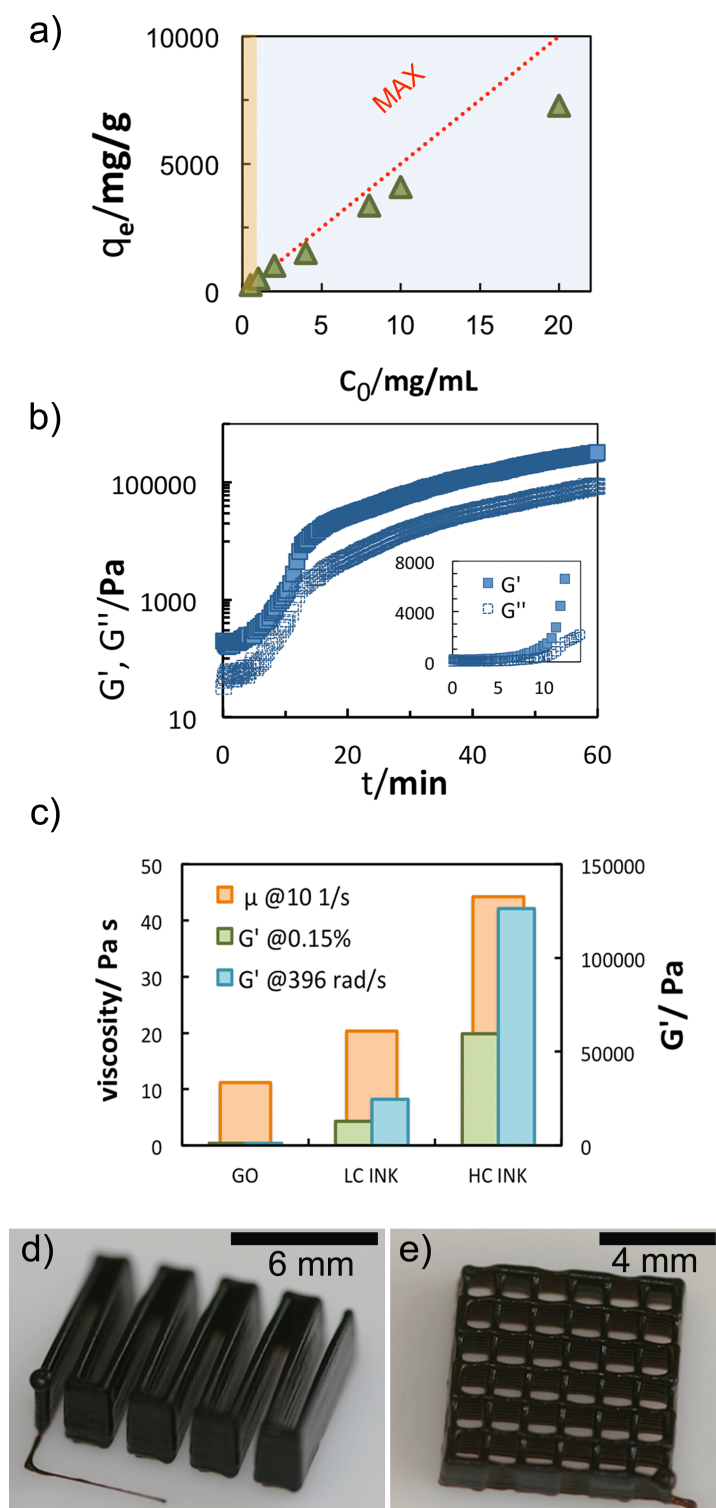


Figure 2. a) The degree of BCS adsorption on GO can be quantified by measuring the attachment of BCS modified with small amounts of rhodamine (BCSr, supporting information) to GO surfaces. The graph shows the adsorption data plotted against the initial BCSr concentrations (C_0). BCSr interacts strongly with graphene oxide. At low initial BCSr concentrations (between 0.5 and 2mg/mL at pH>8, corresponding to GO/BCSr ratios between 4 and 1), all the BCSr molecules are adsorbed on the GO sheets. The dotted line indicates the limit at which all BCS molecules are absorbed on GO. The region highlighted in orange indicates the range of BCS concentrations used in GO/BCS inks for 3D printing. b) Kinetics of self-assembly followed with a time sweep at fixed strain (1%) and frequency (0.1Hz). As

time progresses G δ L decomposes and the pH decreases. During assembly of the inks the pH typically varies from between 8.5 and 10 (before) down to 3.2 and 4.3 (after adding the pH trigger) depending on ink formulation. The viscoelastic properties increase 5 orders of magnitude due to the formation of a 3D network of functionalized GO sheets. c) Histogram showing a comparison of the viscosity and storage modulus (G') of a GO suspension (1.75wt%) without additives (left), a GO/BCS suspension with low graphene oxide concentration (1.75 wt%, LC, middle), and a highly concentrated GO/BCS ink (2.5 wt% GO, HC, right). The viscosity at a shear rate of 10 s^{-1} increases from 10 to nearly 50 Pa s. d-e) 3D-printed graphene structures using robotic assisted deposition. Images showing filament pile and woodpile structures printed through a $150 \text{ }\mu\text{m}$ nozzle with a highly concentrated GO/BCS ink (2.5wt% GO).

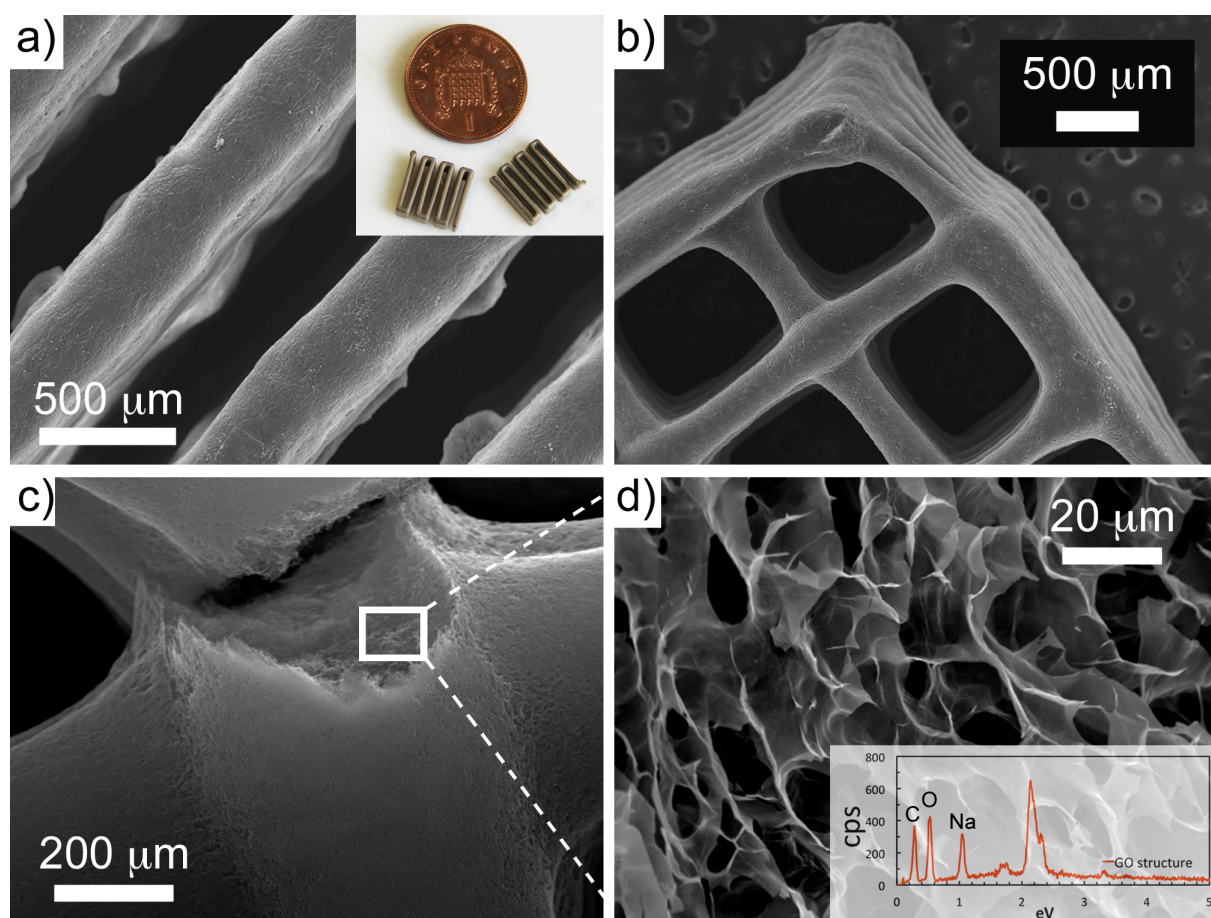


Figure 3. a) Piled up filaments and b) woodpile GO freeze-dried structures (printed through $500 \text{ }\mu\text{m}$ and $150 \text{ }\mu\text{m}$ nozzles respectively) after drying. The woodpile structure exhibits good bonding between layers and good definition. c-d) Fracture of a junction in a woodpile structure printed through $500 \text{ }\mu\text{m}$ nozzle showing the inner microstructure of the printed lines. The lines have densities ranging from 25 to 65 mg cm^{-3} depending on ink formulation (before thermal reduction to rGO). The ice crystals formed during freeze-drying template the formation of a porous architecture inside the printed lines at the microscopic level resulting in highly porous structures with smooth surfaces. The inset in (d) shows an EDS analysis of the freeze-dried structure before reduction. Quantitative EDS analysis before reduction indicate that the dried structures are composed mainly by carbon, oxygen and small amounts of Na (62% C, 35% O, and 3%Na). The sodium impurities come from the NaOH used to regulate the pH during the formulation of the inks.

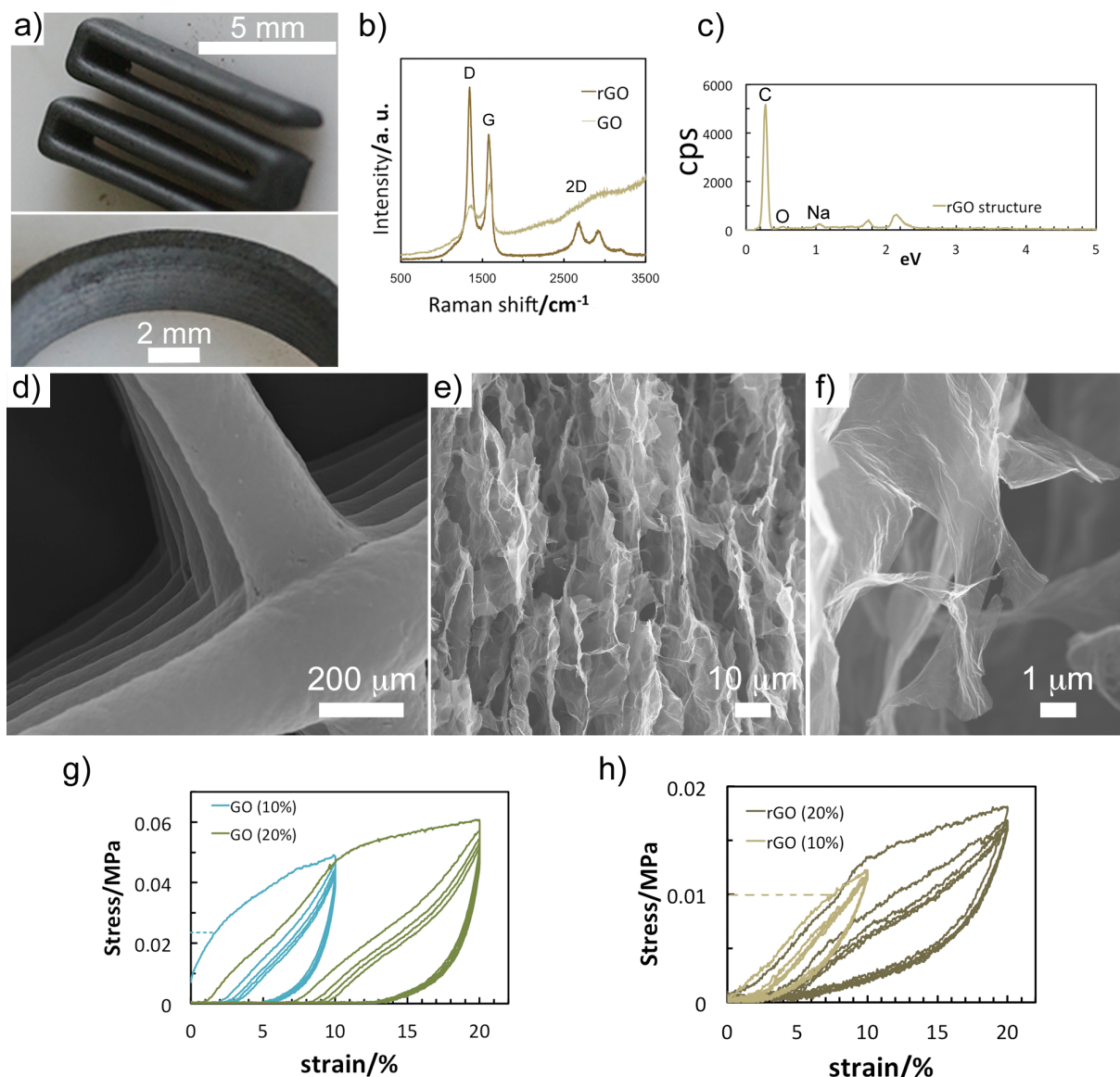
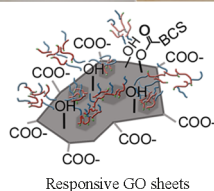
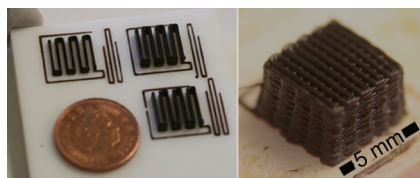


Figure 4. a) Images of rGO filament pile (top) and ring (bottom) structures printed through a 500 μm nozzle after thermal reduction. b) Raman spectra before and after reduction. The analysis after annealing confirms the recrystallization of graphene. The letters D, G and 2D represent characteristic Raman active modes for graphene.^[25] c) EDS analyses after thermal treatment confirm the reduction of GO with small amounts of remaining oxygen and Na impurities (92% C, 7% O, 1%Na). The final densities of the rGO objects range between 6 and 20 mg cm^{-3} . d) SEM image of the woodpile structure printed through a 150 μm nozzle (same as in figures 2e and 3b)) after reduction. The image shows the microstructural detail of a junction between printed lines. There is good bonding and good layer definition in the 3D structure. The filaments retain their shape after reduction. e) The internal microstructure provided by the ice growth is preserved after the annealing treatment. f) High magnification image of the thin ice templated walls. g, h) Comparison of the mechanical properties of a 3D printed structure (piled up filament type, Figure S10c) before ($\rho_{(\text{GO structure})} = 17 \text{ mg cm}^{-3}$) (g) and after ($\rho_{(\text{rGO structure})} = 6 \text{ mg cm}^{-3}$) (h) the reduction process. Non-reduced parts have higher yield stress (dashed lines in the graph, $\sim 0.025 \text{ MPa}$ and 0.01 MPa for GO and rGO respectively) and Young modulus ($E_{\text{GO}} = 0.84 \text{ MPa}$, $E_{\text{rGO}} = 0.13 \text{ MPa}$) due to the presence of BCS linking the graphene sheets.



‘Responsive graphene oxide sheets form non-covalent networks with optimum rheological properties for 3D printing. These networks have shear thinning behavior and sufficiently high elastic shear modulus (G') to build self-supporting 3D structures by direct write assembly. Drying and thermal reduction leads to ultra light graphene-only structures with restored conductivity and elastomeric behavior.’

Keywords: 3D printing, graphene, responsive polymers, and functionalization.

Esther García-Tuñón*, Suelen Barg*, Jaime Franco, Robert Bell, Salvador Eslava, Eleonora D’Elia, Robert Christopher Maher, Francisco Guitian, and Eduardo Saiz

Printing in three-dimensions with graphene